Column observations of NOx and OVOC over California during CalNex and CARES

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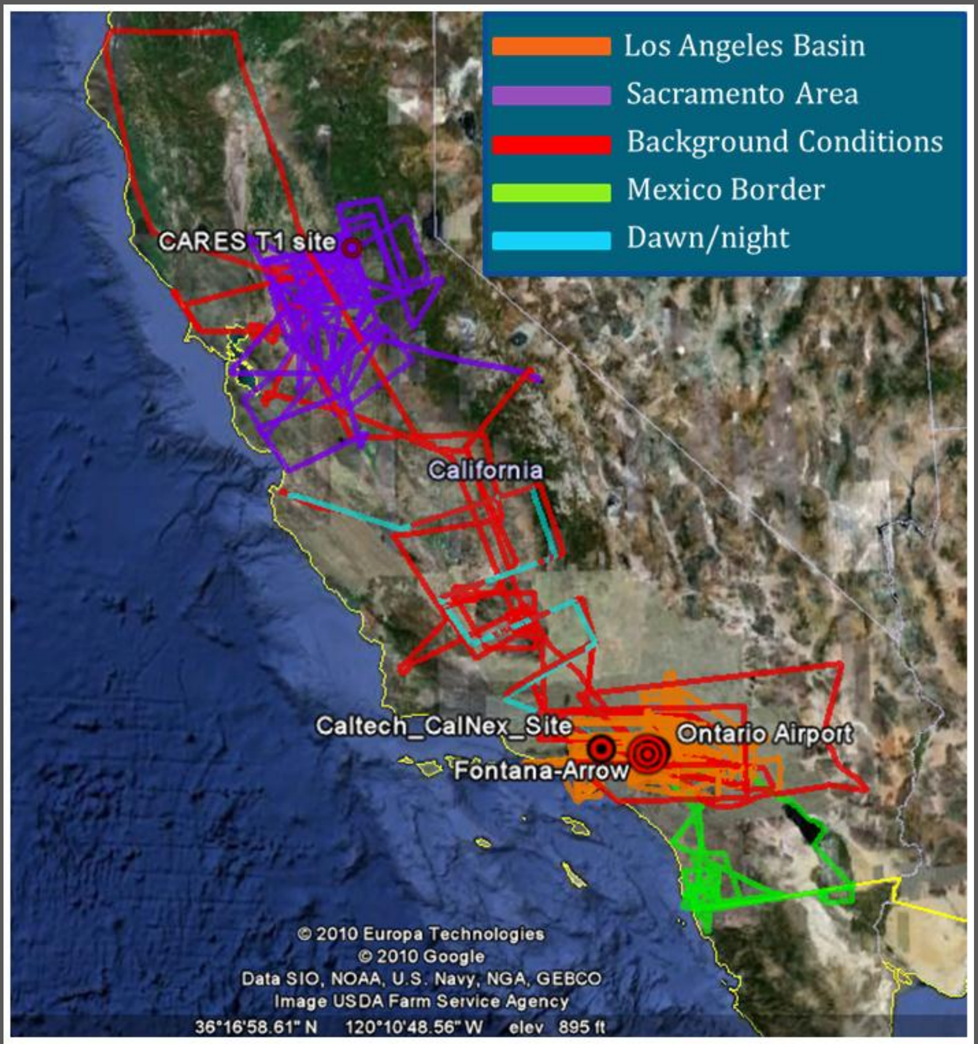
Objectives:
Assess boundary conditions , NOx emissions, and OVOC abundance (HOx, SOA)
Map 2D distributions and vertical profiles (SoCAB, Central Valley, Northern California)
Assess pollutant transport (splitting of flows, mountain passes, high deserts)
Enhance value of ground sites (Caltech, Bakersfield, Cool)

Overview CALNEX and CARES activities



CU Airborne MAX-DOAS:

- May 19, 2010 – July 19, 2010
- Total of 52 flights
- flight duration: up to 4.5 hours
- 207 total flight hours

CU Ground MAX-DOAS:

- Caltech (May 15-Nov)
- Fontana Arrows (May 15-Nov)
- CARES T1 (June 11-28)

CU LED-CE-DOAS:

- Caltech (May 14 - June 16)
- e.g., Glyoxal (15ppt@1min)

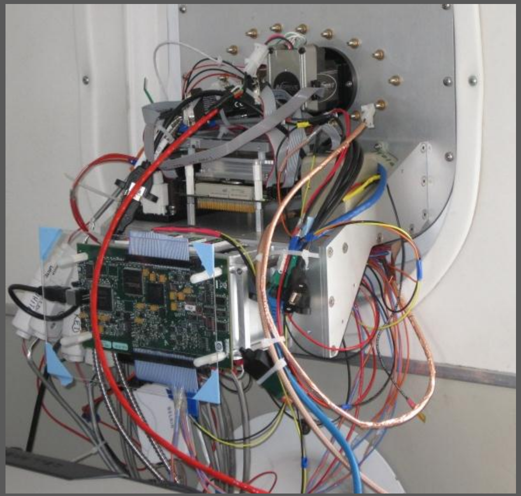
Posters: Baidar et al. (AMAX-DOAS), Ortega et al. (GMAX-DOAS), Thalman et al. (LED-CE-DOAS)

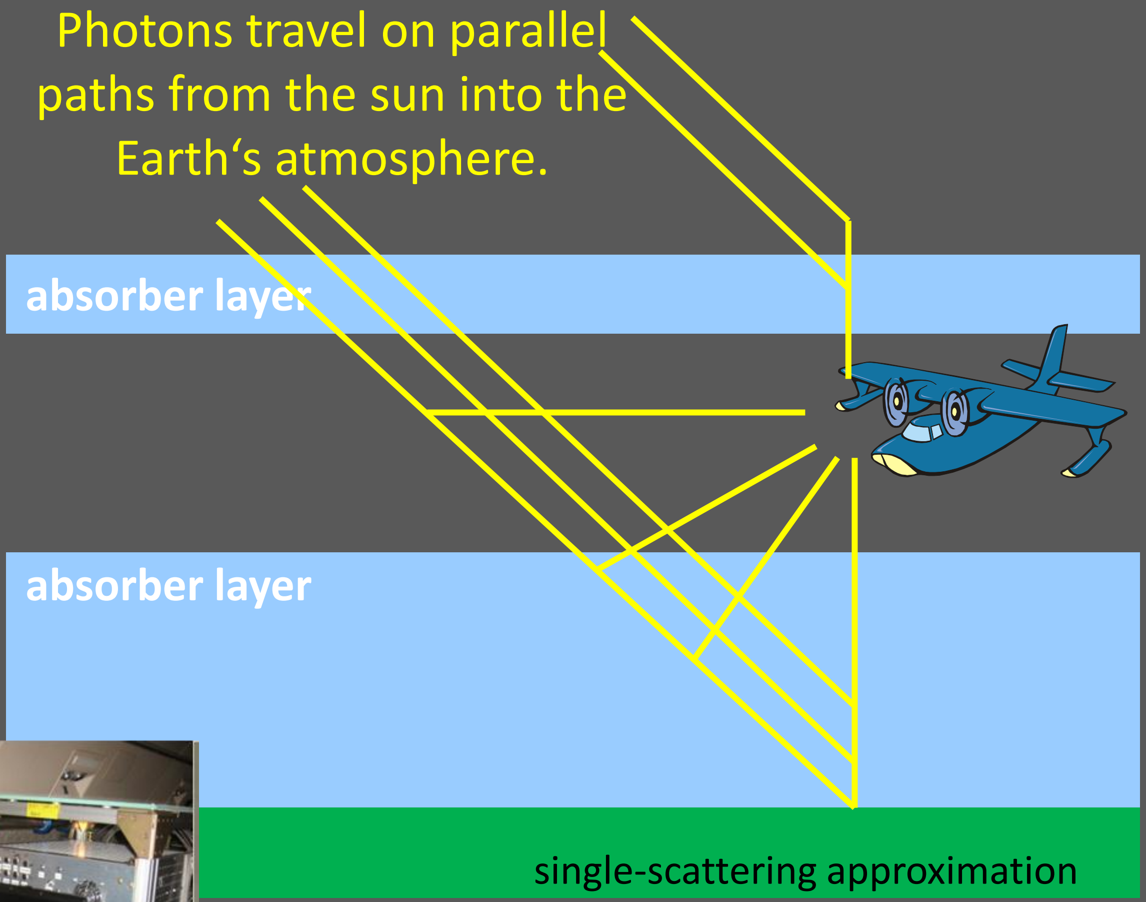
NOAA Twin Otter – optical remote sensing

- Primary instruments:
  - Downward-looking ozone and aerosol Lidar (TOPAZ = Tunable Optical Profiler for Aerosols and oZone)
  - U of Leeds Scanning Doppler Lidar
  - CU Airborne Multi-Axes Differential Optical Absorption Spectroscopy (CU AMAX-DOAS) Instrument
- Additional instruments:
  - In situ O_3, temperature, pressure
  - Radiometers (surface temp, albedo)
  - CU motion compensation system

CU AMAX-DOAS instrument & concept

- Rotating prism telescope
- Real-time motion compensation
- 2 synchronized spectrometers/CCDs

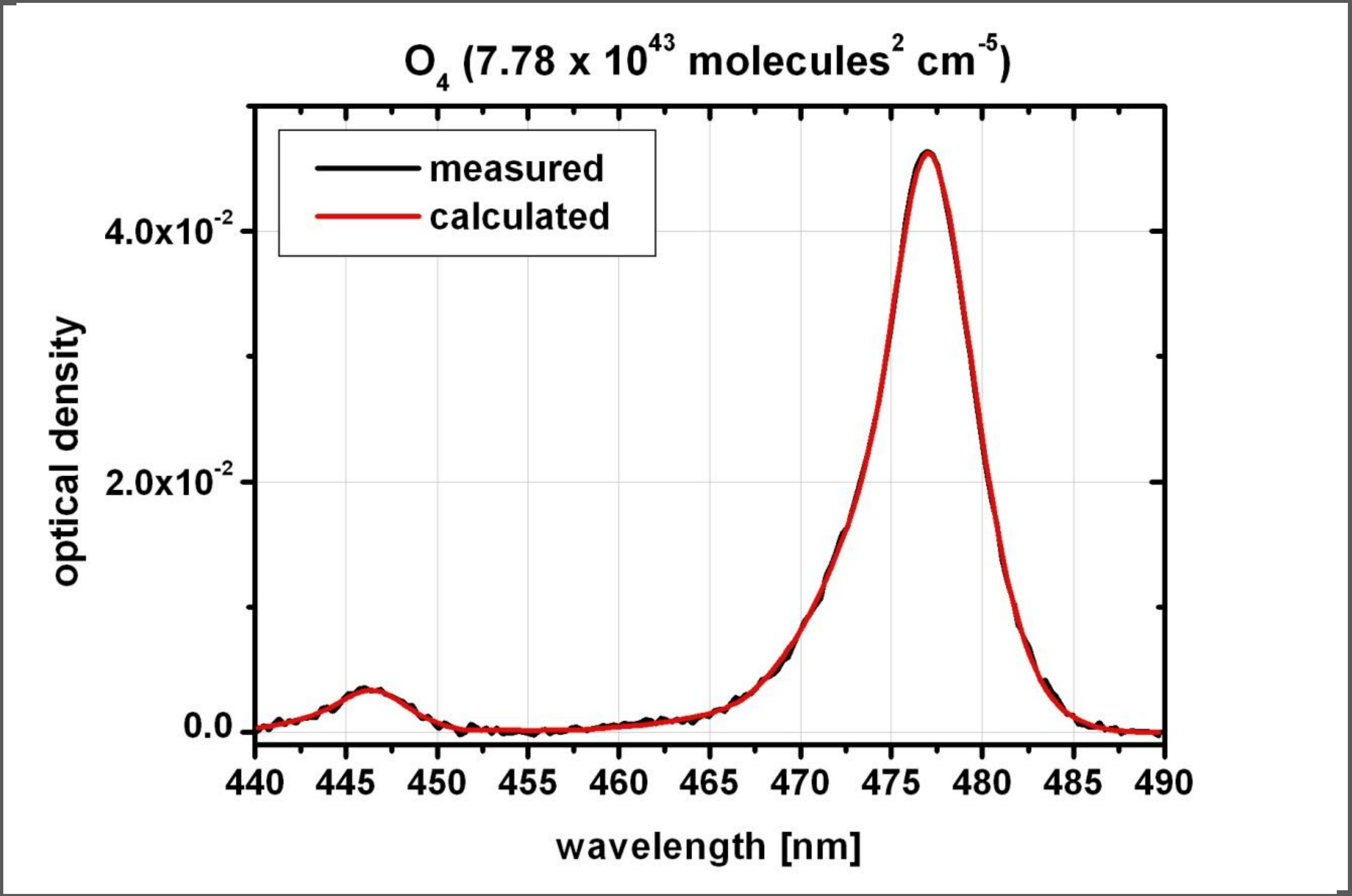




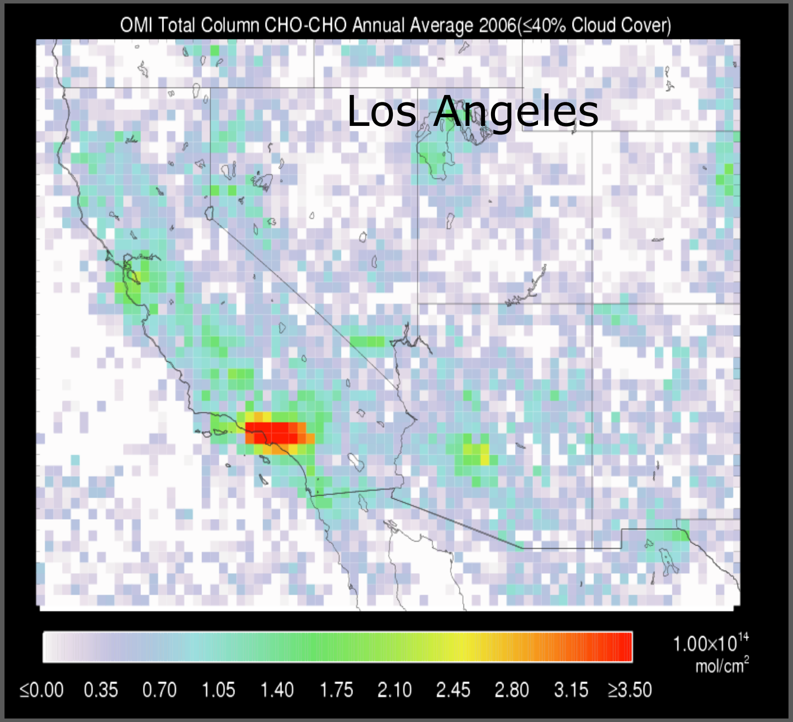
- ***Retrieval:***

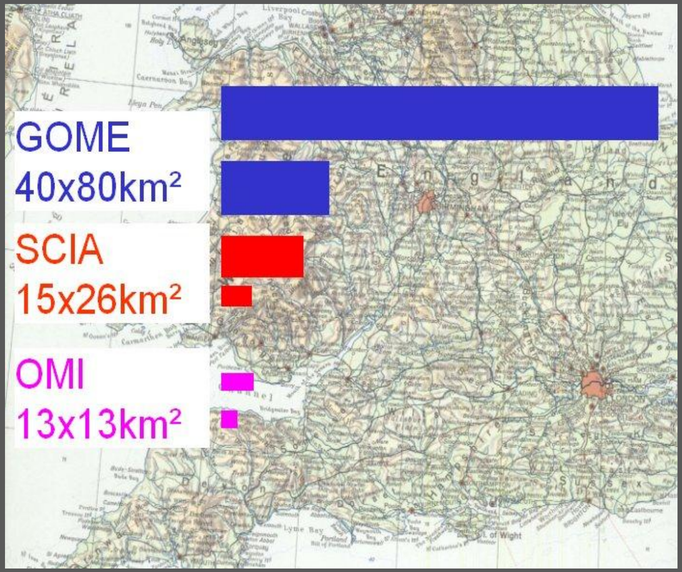
Measured spectra are analysed with the *DOAS method*. This yields the integrated absorber density along the light path: the so-called *slant column density*

Spectral proof of measured gases



Sampling extended spatial Scales

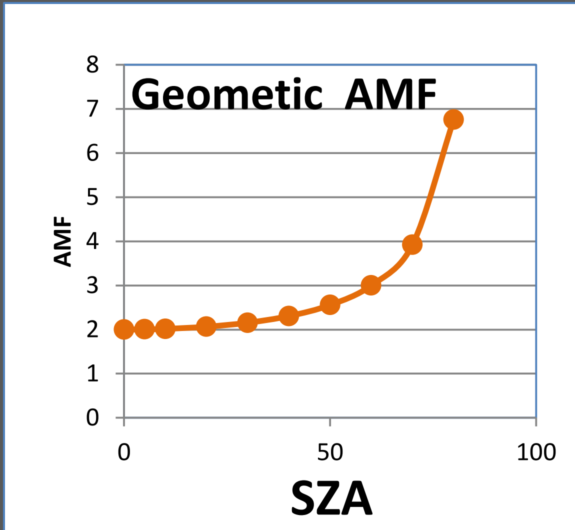


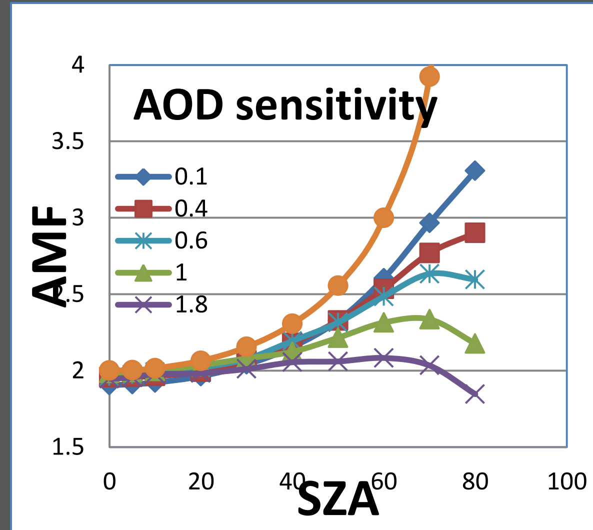


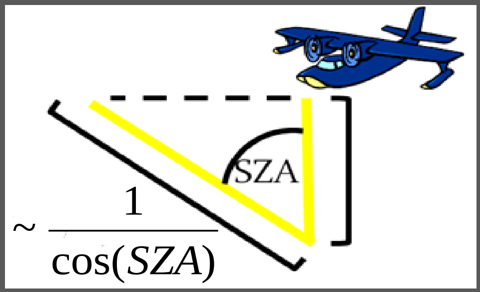
WRF-Chem, UCD-CIT: 4x4km^2

- CU AMAX-DOAS sampling strategy consisted in sequential zenith-to-NADIR scanning (2 sec/spectrum). NADIR resolution: 1km along track.
- Inherently averaged column measurement over PBL, or 20-60km forward view. This is directly comparable to scale probed from satellites.
- Mobile column observations complement in-situ measurements, and bridge scales between ground-based networks and atmospheric models.

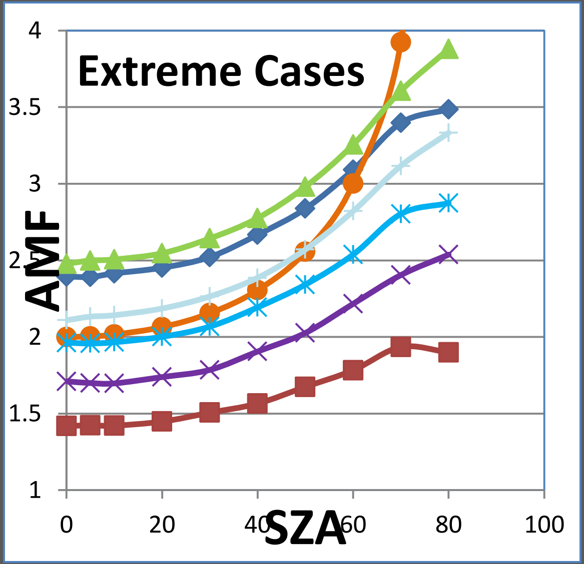
Sensitivity studies geometric AMF







Geometric Approximation



	Realistic Conditions	Maximize AMF	Minimize AMF
SSA	0.94	0.99	0.70
Albedo	0.10	0.25	0.05
g-parameter	0.68	0.60	0.75
AOD	<0.4	0.4	0.4
SRAA	40	40	40

- For SZA < 60 deg a conservative estimate of error is <30%

Surface Albedo

Preliminary data RF#46

Measurement principle:

- Differential Irradiance
- atmospheric correction

CALNEX upgrade 2010:

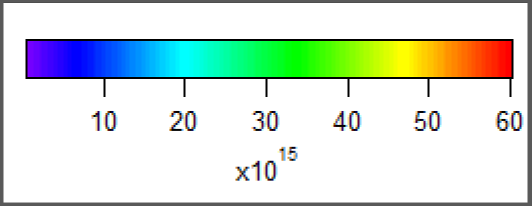
- 4 channels

  360nm
  478nm
  630nm
  868nm

$\left.\begin{array}{l}360\text{nm}\\478\text{nm}\\630\text{nm}\end{array}\right\}$ O_4 bands

Case study: South Coast Air Basin

Observations
RF#46, 7/16, AM



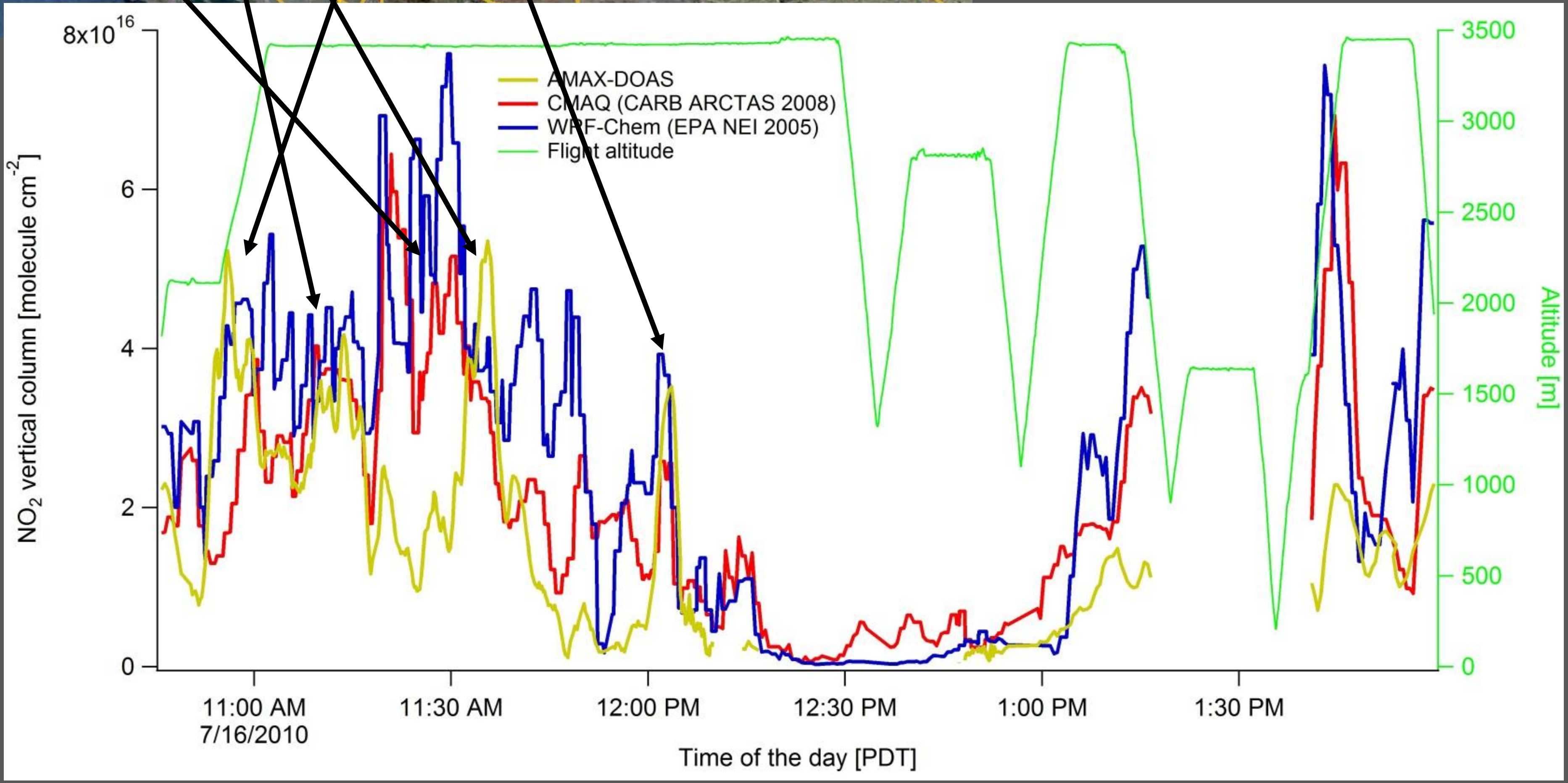
WRF-Chem Model
(EPA NEI 2005)

CMAQ Model
(ARB ARCTAS 2008)

- Observed NO_2 VCD is lower than predicted by both models.

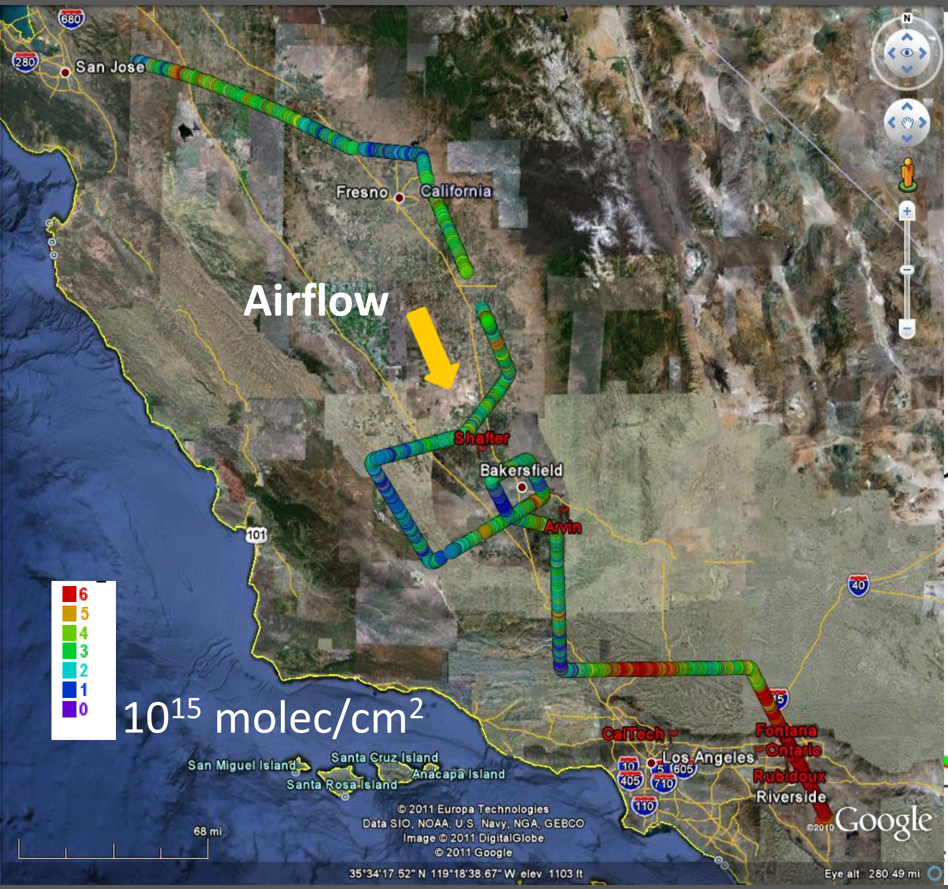
Case study South Coast Air Basin (cont)

- Measurements show NO2 transport towards East
- Both models show flow primarily into Santa Clarita area
- Differences over downtown

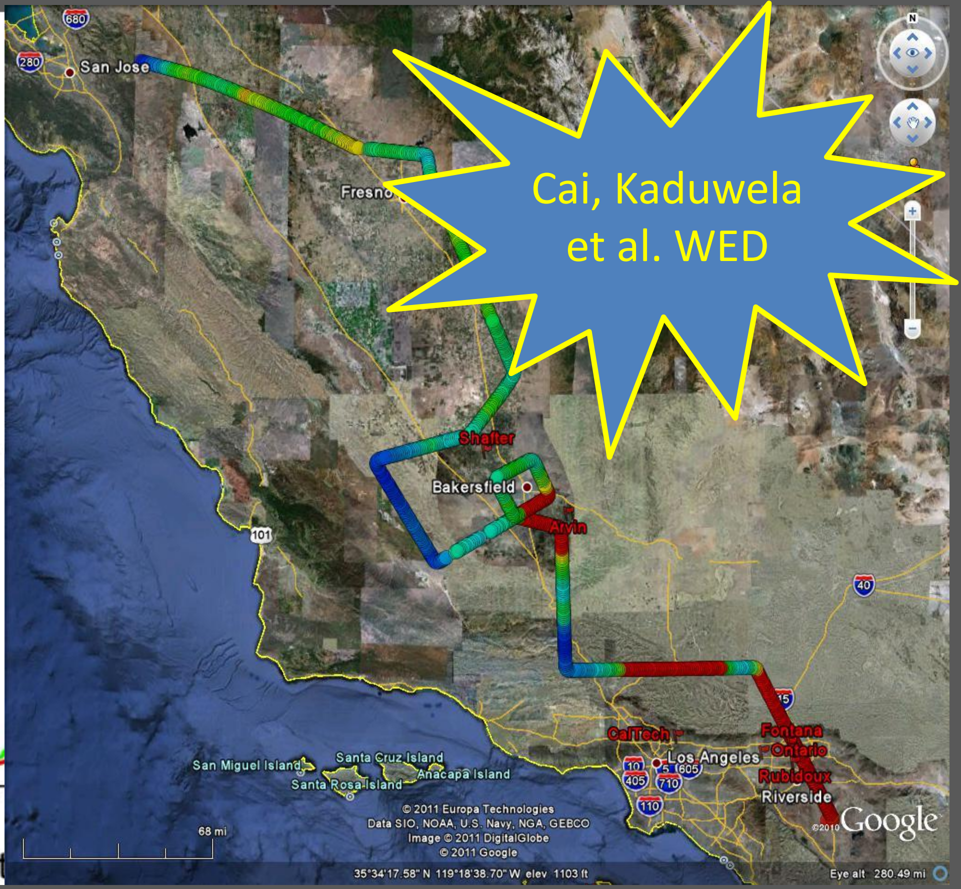


NO_2 VCD mapping Central Valley

Observation (Flight#34, 6/29)



CMAQ Model (ARB ARCTAS 2008)



- Locations of elevated NO_2 VCD match reasonably well
- Quantitative agreement only over Central Valley

Comparison of Emission Inventory in LA box

Inventory	NOx [mol/km^2/hr]	CO [mol/km^2/hr]
EPA NEI 2005	100	1197
Millstein and Harley, EST (Yr 2005)	61	450
CARB ARCTAS 2008	73	440
Projected for 2010*	34	

* projection based on 9%/year decrease 2005-2008 (Russell et al., 2010)

Acknowledgement:
Stu McKeen, Greg Frost, Dev Millstein, Rob Harley for providing emission information.

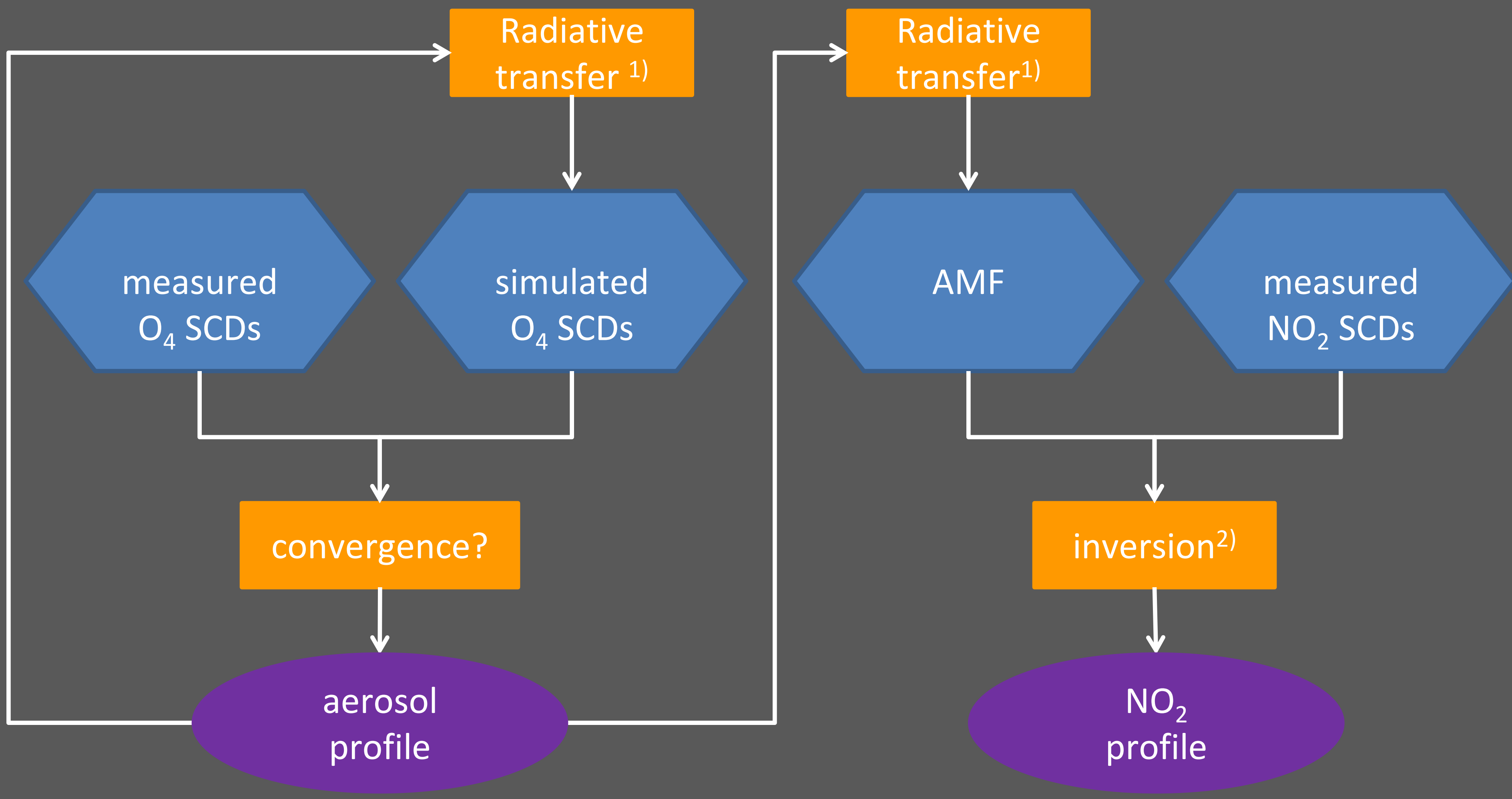
Conclusions: NO2 horizontal mapping

- NO2 VCD is reasonably well constrained by the geometric AMF approximation (error < 30%, likely much smaller)

- For arbitrarily selected case studies NO2 VCD agrees well in Central Valley, but not downwind of urbanizations, where NO2 emissions are observed much lower than predicted (factor 2-5)

- Strong NO2 gradients are observed within SoCAB. NO2 transport into Santa Clarita was lower than predicted, leading to instances where NO2 was observed higher than predicted.

Vertical profiles: Non-linear Optimal Estimation

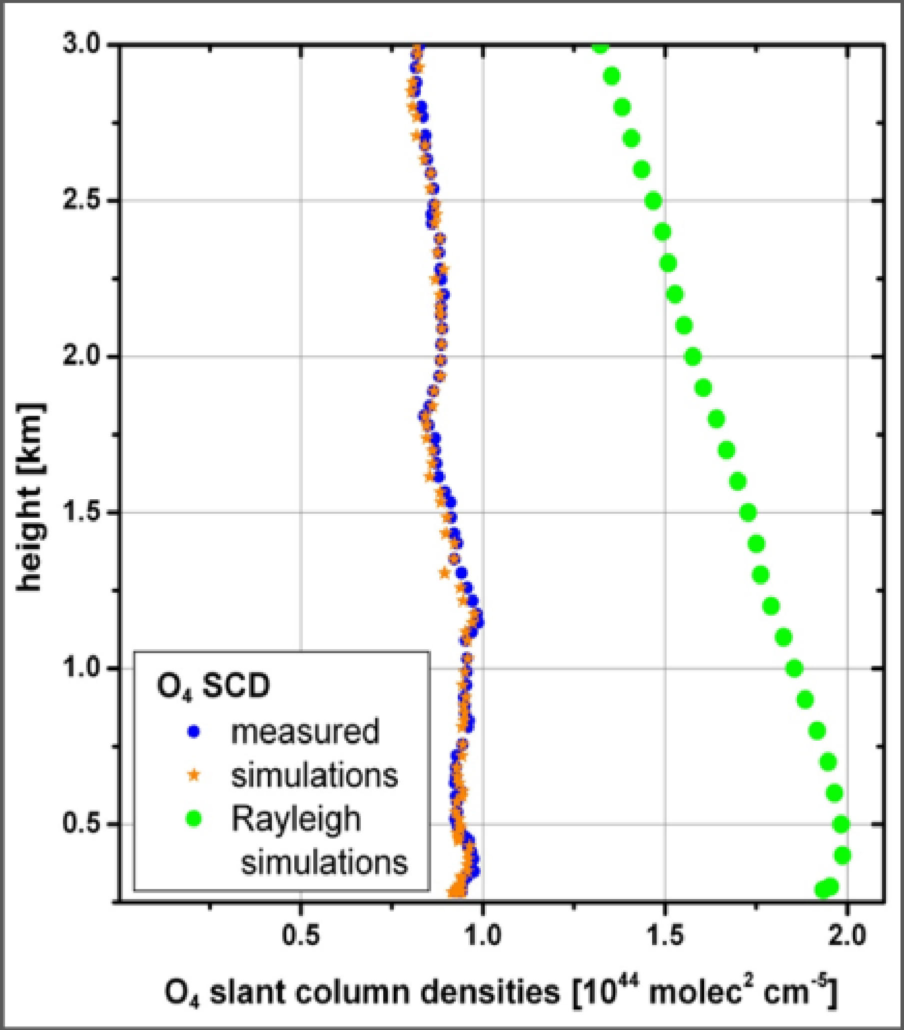


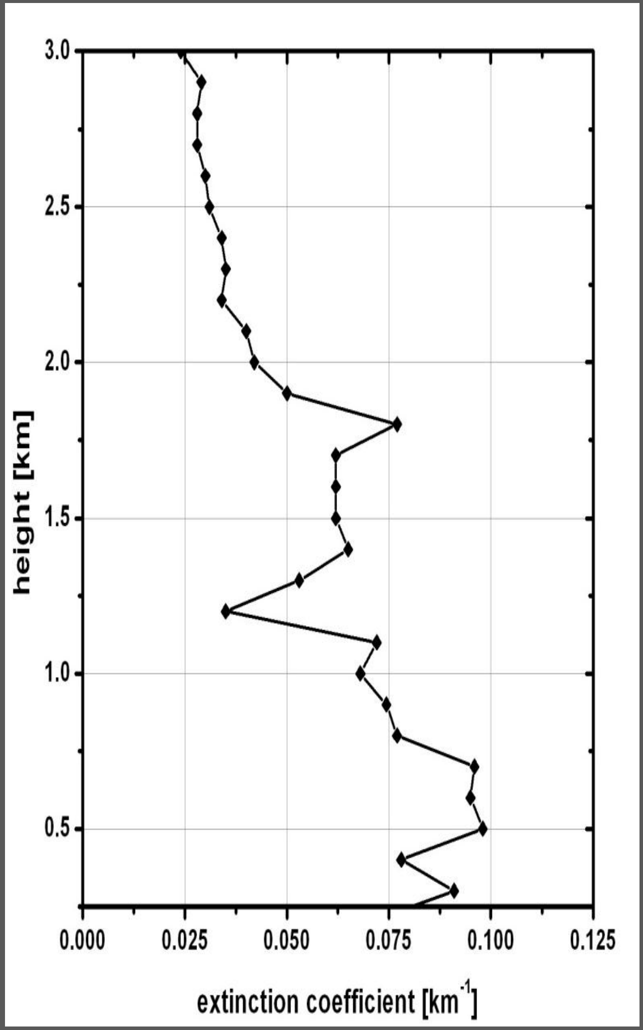
[1)] http://rtm.iup.uni-heidelberg.de/McArtim

[2)] Rodgers (2000)

Example: NO_2 and extinction vertical profile

July 18, 2010 (6:20-6:29 am)





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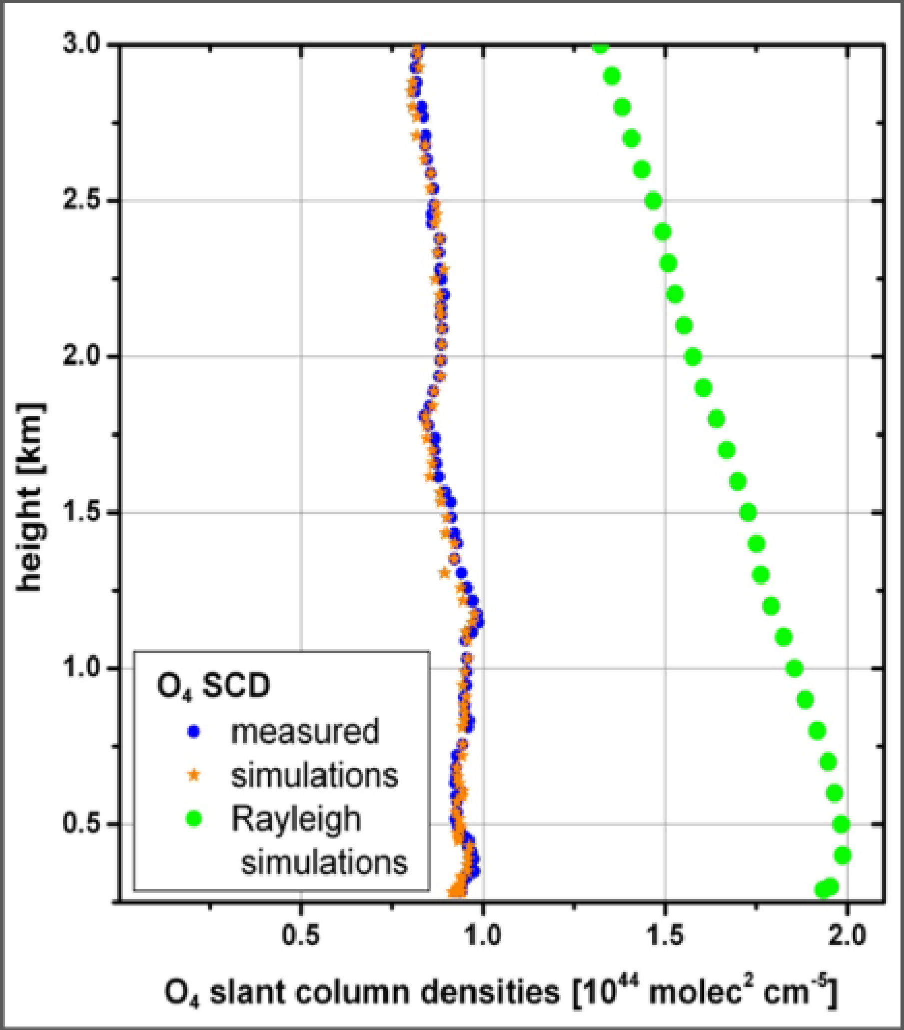
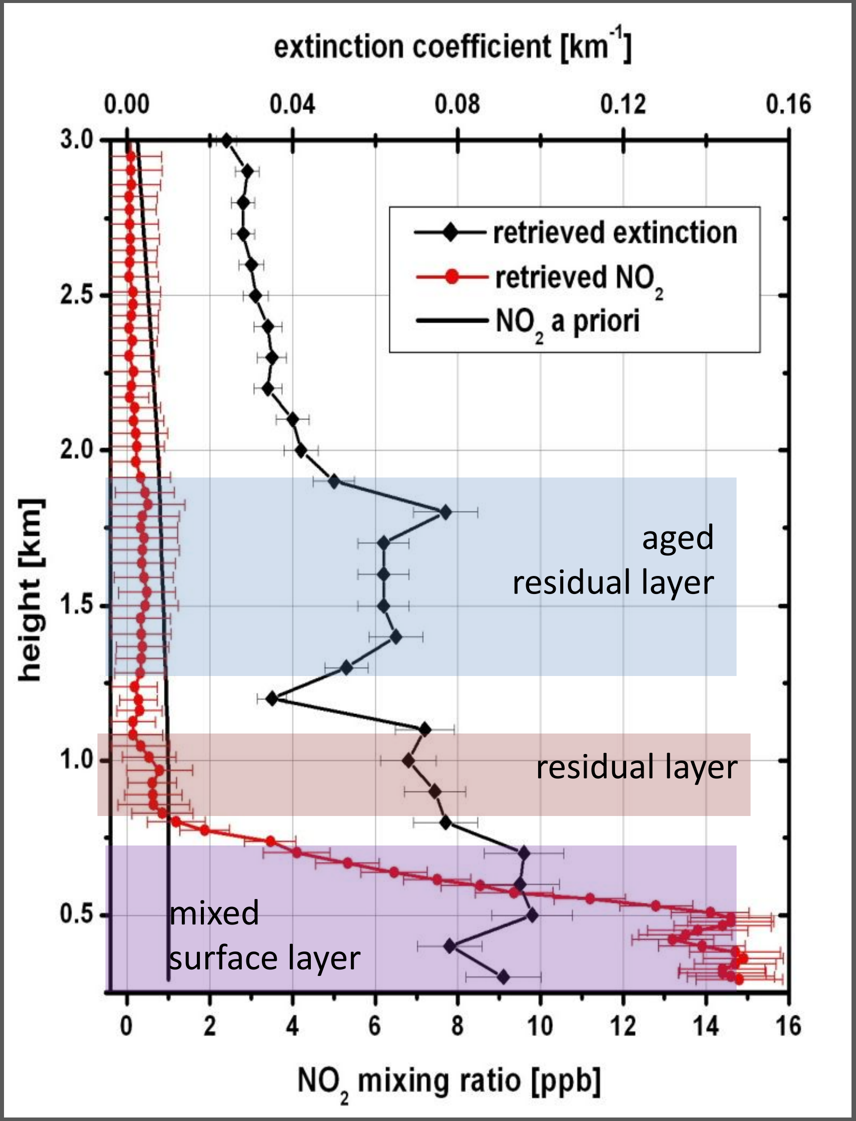
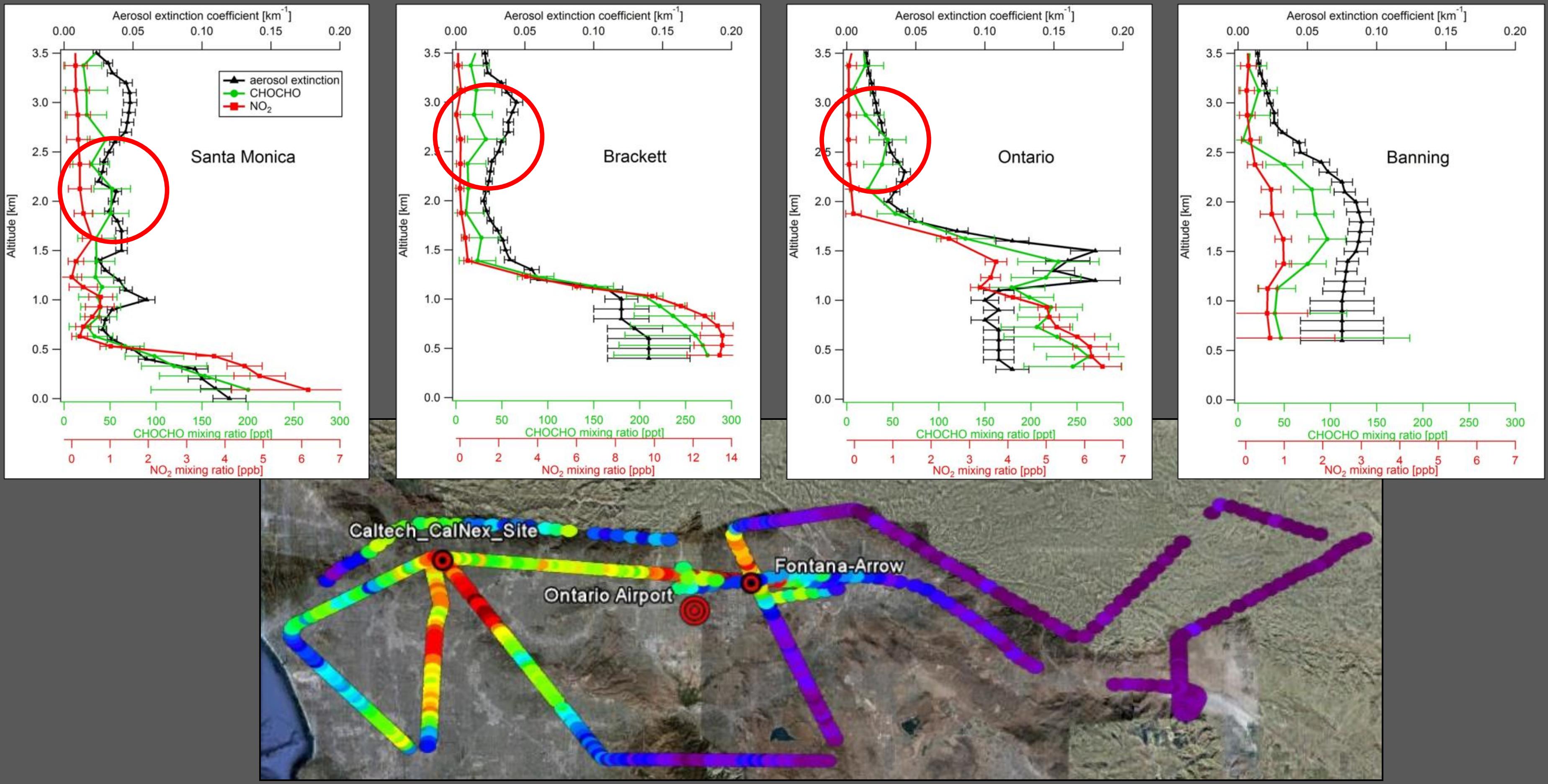




NO_2 and CHOCHO vertical distributions



- PBL increase from West to East of the SoCAB
- A heterogeneous airmass !
- Glyoxal in FT indicates rate of VOC oxidation outside PBL

Conclusions and Outlook

- CU AMAX-DOAS is a unique instrument to map 3D distributions:
  - First systematic MAX-DOAS implementation from aircraft
  - Motion compensation challenge overcome, albedo, stratospheric photon path
  - Aerosol extinction and numerous trace gases (also H_2O, BrO, IO, OClO)
- Innovative means to address scaling problem:
  - Fills gap in mobile observational capabilities between in-situ, satellites and atmospheric models
- NO2 emissions testing points to a need to adjust inventories
- NO2 as a tracer for plume transport (splitting of flows)
- Glyoxal in the ‘free troposphere’

- Outlook:
  - Compare with our ground MAX-DOAS column observations
  - Synergies with TOPAZ LIDAR to constrain Ox = NO2 + O3 column
  - Synergies with HALO LIDAR to constrain fluxes across boundaries (box budgets)
  - Refine RTM: Assimilate albedo
  - Atmospheric model testing: towards constraining the rate of VOC oxidation
  - Satellite comparisons
  - Add value to ground sites?

Funding: CARB 09-317, NSF-CAREER

Science Objectives

Emissions

- How can we improve the emissions inventory for NOx and aerosol precursors?

Chemical Transformation and Climate Processes

- What are the sources and physical mechanisms that contribute to high ozone concentrations aloft?
- Are there significant differences between Central Valley and South Coast Air Basin precursors or ozone formation chemistry?
- What are the most important formation processes for secondary organic aerosol?

Transport and Meteorology

- What are proper oceanic boundary conditions for coastal and regional atmospheric chemistry modeling?
- How best can we characterize and model air flow over coastal waters and the complex terrain of California?
- What are the important transport corridors for key chemical species and under what conditions is that transport important?